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CORROSION EMBRITTLEMENT OF DURALUMIN

II. ACCELERATED CORROSION TESTS AND THE BEHAVIOR OF  
HIGH-STRENGTH ALUMINUM ALLOYS OF  
DIFFERENT COMPOSITIONS

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I. Introduction

As shown in the previous report, light aluminum alloys of the duralumin type, that is, wrought alloys whose properties can be improved decidedly by heat treatment and which, for this reason, are widely employed in aircraft construction, at times have shown evidence of a lack of permanence and reliability while in use. This lack of permanence has been shown to be the direct result of an intercrystalline corrosive attack which, although starting at the surface of the material, gives very little evidence in the changed appearance of the corroded part of the extent of the attack and the seriousness of the resulting impairment of the properties of the material. This form of deterioration of duralumin is most serious in the case of sheet material. The tendency toward this change, according to the observations which have been made, has been exhibited by only a relatively small amount of the total quantity of sheet duralumin which has been put into use. However, such a change, whereby a

sheet may be converted from a strong ductile material into a very weak brittle one with no accompanying marked change in the external appearance, is of such an insidious nature that, until reliable information is available, all duralumin must be regarded, more or less, with suspicion. To obtain such information so that precautionary measures to guard against possible deterioration of this type may be taken, a comprehensive investigation was necessary. The results of this investigation form the basis of this series of reports (Reference 1). The work has been carried out at the Bureau of Standards in cooperation with the National Advisory Committee for Aeronautics, Bureau of Aeronautics of the Navy Department, and Army Air Corps. The leading manufacturers have also participated in the investigation by furnishing practically all of the materials needed. The investigation, which was started in the latter part of 1925, is still in progress and final and complete answers have not been reached on all points concerning the permanence of duralumin in service. The information which has been obtained, however, is of very considerable value to both manufacturers and users of aircraft and its publication at this time would seem to be warranted although possibly some of the statements made in this progress report may be modified slightly in the light of future results.

## II. Materials and Method of Test

### 1. Material

Most of the tests which have been carried out in the investigation of intercrystalline corrosion have been made upon 14-gauge sheet furnished by two manufacturers (referred to below as A and B), as representative of their products. The composition of these materials is given in Table I, although it should be mentioned that the composition may vary slightly from lot to lot.

The first lot of material supplied by each of the two manufacturers, though representative of the practice regularly followed, was prepared especially for this investigation and a careful record of the various stages of manufacture was kept and furnished with the material. The succeeding lots of material furnished by the manufacturers were taken, except in a few cases of material of special composition, from the regular stock. The behavior of the material of these later lots was in all essential respects the same as that furnished with a complete "metallurgical history." The materials used in the earlier tests were representative of annealed, heat-treated, and heat-treated-and-cold rolled sheet. In later tests, however, the heat-treated material was used almost exclusively.

The tensile properties of the materials in the initial or uncorroded state are given in Table II.

TABLE I

Composition of Aluminum Alloys Used in Corrosion Tests

Elements of composition determined	Manufacturer A	Manufacturer B
Cu	4.1%	3.9%
Fe	.34%	.51%
Mn	.51%	.58%
Mg	.61%	.60%
Si	.32%	.31%
Cr	Not detected	Less than .02%
Sn	" "	Not detected
Ni		
Zn		
Ca		
Al (diff.)	94.12%	94.08%

Various other alloys, some of them differing rather decidedly in composition from those listed above have been also used in different phases of the work. These will be referred to later.

TABLE II

Tensile Properties of 14-Gauge Sheet Duralumin in  
Its Initial or Uncorroded Condition

Manu- facturer	M a t e r i a l	Tensile properties*		
		"Yield" point (by graph)	Ult. ten. strength	Elongation (2")
A	A, annealed	1b./in. <sup>2</sup> 12,000	1b./in. <sup>2</sup> 32,500	per cent 20.0
	HT, heat-treated (quenched-and-aged)	40,000	61,000	23
	TR, cold-rolled after heat-treatment	63,000	72,500	8
B	A, annealed	13,000	27,500	18
	HT, heat-treated	37,000	62,000	21
	TR, cold-rolled after heat-treatment	59,000	71,500	7

## 2. Method

The method commonly used for evaluating corrosion tests consists essentially in the determination of the loss of weight of the corroded specimen per unit area of exposed surface for a stated period of time. If desired, this result can be expressed in terms of the thickness of the metal layer removed and thus an estimate can be formed as to the effect of the corrosive attack on the tensile strength of any given member. Such a method is applicable to corrosion of the first type de-

\*Each value given is the average of three determinations.

scribed above. It is obvious, however, from a consideration of the structural aspects of duralumin corroded according to the second method, that, in such a case, the loss-of-weight determination would furnish no criterion by which the full effect of the corrosive attack on the properties of the material could be measured.

The method used in the investigation consisted in the corrosion of full-size tension bars of the material, the average properties of which in the initial or uncorroded state had already been determined. For each test a number of specimens were used, individual bars being removed successively from the test after a known period of corrosion and tested in tension. Although this method of carrying out corrosion tests on full-size tension bars has previously been described (Reference 2), its use as a practical means of corrosion testing does not seem to have been followed to any extent.

Figure 2 shows a diagram of the tension specimen used.

It might be inferred from the preceding report, that the two types of corrosion in duralumin always occur independently of each other. This is not so, however. The two may be more or less related and this is more often the case in accelerated laboratory tests than in the more "natural" form of corrosion such as occurs during atmospheric exposure. It was necessary, therefore, that the structure of the corroded specimens be examined in order to determine which of the two types of corrosive

attack predominated and to which the observed change in the properties of the metal should be ascribed.

Occasional wetting followed by a period during which the metal surface is permitted to dry off is more comparable to the conditions which obtain in aircraft service than a continual wetting of the surface would be. This fact determined, in large measure, the method used in carrying out the corrosion tests. The tension specimens, supported horizontally on edge in a supporting framework formed out of glass rod, were lowered periodically into the corrosive solution and then withdrawn into the air. The apparatus used is shown in Figure 3. By means of a clock, with suitably spaced mercury pits through which electrical contact was made by the minute hand, the motor operating the crank arms to which the baskets containing the specimens were attached was started every 15 minutes and operated long enough to permit the lowering of the specimens into the solution and their withdrawal into the air.

A few tests were also carried out by continuous immersion as well as by means of the "spray test." In the latter, the specimens were exposed continuously to the corrosive solution in the form of a fog or mist within a closed chamber. The results obtained were of the same general nature as those obtained by the repeated immersion method, but a longer exposure period was necessary in order to obtain comparable results. Likewise the few tests made by the simple immersion method gave results

comparable to those by repeated immersion but the attack was somewhat slower than was the case with the repeated immersion method.

### III. Results of Accelerated Laboratory Corrosion Tests of Sheet Duralumin

#### 1. Description of Tests

In order that accelerated tests may throw any light on the question of the embrittlement of duralumin, the following requirements must be met: (1) the corrosive attack of the metal must be intercrystalline in nature, at least in large measure; and (2) the test method and specimen must be such that the effect of the corrosive attack on the properties can be readily evaluated. The latter requirement was fulfilled by carrying out the tests on full-size tension specimens as described in the foregoing section. In order to fulfill the first requirement, however, considerable "reconnaissance" work was necessary.

Examples of embrittlement of sheet duralumin which had been reported to the Bureau of Standards could in most cases be associated with the presence of chlorides either as sodium chloride in the marine or sea-coast atmosphere or as a solution such as calcium chloride which had accidentally been spilled on the material. Calcium chloride solution was the first one employed in the laboratory tests. The results obtained, which are summarized in Figure 4, showed that considerable embrittlement of

sheet duralumin can be produced by corrosion by this solution and microscopic examination showed further that the corrosive attack was in large measure, of the intercrystalline type (Fig. 5). The relative intensity of the attack of the different forms of immersion tests and of the spray test is also shown by these results.

In Figure 4 and other similar figures, the progress of the attack is shown best by the decrease in elongation (that is, ductility). The attack has to be quite far advanced, as a rule, before the tensile strength is lowered very materially. The shaded blocks are, therefore, the more significant ones.

In order to obtain changes in the tensile properties of the magnitude shown in Figure 4, a rather prolonged corrosive attack was necessary. In most cases, the corrosion period was extended to 40 days. Obviously, for an accelerated laboratory test, a much shorter period than this would be very desirable. It is well known that the addition of an oxidizing agent to an acid will accelerate the corrosive attack on most metals which are exposed to the acid. Some attempts have been made to utilize this fact in corrosion tests, for example, Wernlund (Reference 3) had described the use of a mixture of hydrogen peroxide and acetic acid for the testing of zinc coatings, and Mylius (Reference 4), the addition of hydrogen peroxide to a solution of sodium chloride for determining the corrodibility of aluminum. Mylius showed that the corrosion rate of aluminum as measured by the

loss-of-weight method was much greater with the oxidizing solution than with a plain solution of sodium chloride. Preliminary tests on sheet duralumin with a solution of this kind suggested the desirability of its use in this investigation since a pronounced embrittlement could be produced within a few days and furthermore microscopic examination showed that the attack was largely intercrystalline in its nature (Fig. 1). In Figure 6 are summarized the results of a number of tests in which this solution was used, the accelerating effect of the oxidizing reagent being very evident. Further tests showed that a somewhat milder intercrystalline attack could be produced by a solution of hydrogen peroxide alone. Evidently hydrogen peroxide is not unique in its accelerating effect on the corrosion of duralumin as was shown by the results obtained by the use of chlorine water as an oxidizing agent (Fig. 7). Potassium persulphate was also found to have a very marked accelerating effect but in this case the corrosive attack was so localized that the use of this oxidizer was not considered to be practicable as a laboratory corrosion test.

Other reagents both with and without the addition of hydrogen peroxide were used in corrosion tests; nitrates, carbonates, and sulphates, as well as other chlorides, were tried. In the heat treatment of duralumin, fused-nitrate baths are very often used and films of the fused salts not infrequently persist on the metal surface after quenching; hence, the importance of de-

termining whether or not corrosion may be promoted by this cause. Carbonates are often formed as a result of atmospheric corrosion and sulphates are found to a very appreciable extent in sea water. From the results, which are summarized in Figure 7, it will be seen that of the various solutions used, chlorides constituted the only class which actively accelerated the corrosion of duralumin. The attack was in all cases of the intercrystalline type. A few simple immersion tests on the same kind of metal in solutions of iodides and bromides (sodium and potassium salts in each case) gave results showing that the other halogens behave similarly to chlorides. According to the microscopic structure of the corroded specimens the three halogen solutions were placed in the following order with respect to the severity of attack: iodides, bromides, chlorides, the last being the most severe.

The statement has been made (Reference 5) that dilute sodium chloride solutions are more severe than more concentrated ones; for example, that a solution of 1/6 the concentration of sea water is more severe in its attack than sea water. Statements to the effect that sodium chloride is more active than other chlorides have also been made. Tests were made with sodium chloride solutions of the following concentrations: approximately 11.5, 5.8, and .6 per cent (2N, N, N/10). (Sea water has an average sodium chloride content of 3.33 per cent.) The results (Fig. 8) did not indicate any pronounced differences which could be attributed to the concentration of the solutions. A potassium

chloride solution was found not to differ much in its attack from a sodium chloride solution of the same concentration. Ammonium chloride, however, proved to be very corrosive - a simple solution of this chloride being as active as one of the same chloride to which an oxidizer had been added. Since duralumin in service may come in contact with ammonium compounds resulting from the decomposition of animal waste products, it was considered advisable to investigate the possible corrosive effect of solutions of other ammonium compounds. The results, which are summarized in Figure 8, indicated that only in case of chlorides, are ammonium compounds to be regarded as a cause of severe corrosive attack.

## 2. Some Factors Affecting the Accelerated-Corrosion Tests

### (a) Method of Cleaning Specimens

The results obtained on sheet duralumin corroded by means of the sodium chloride-hydrogen peroxide solution or other accelerated corrosion tests are not to be regarded as truly quantitative, that is, in the strict sense of the word. Considerable variation in the results for different specimens, even with those corroded side-by-side in the same solution was not uncommon. The character of the corroded surface would suggest that this might be expected. The corroded specimens usually had a "spotty" appearance, that is, the surface was not uniformly corroded all over but the attack was more intense at certain points.

than at others (Fig. 5). In order to determine whether the non-uniformity of the corrosive attack was related to or determined by the method by which the specimens had been cleaned prior to corrosion, several sets of specimens were cleaned by different methods and then all were corroded under as nearly uniform conditions as possible. The cleaning methods used included the following: rubbing with a cotton swab wet with alcohol followed by rinsing with ether; the same with carbon tetrachloride followed by ether; etching with a one-per-cent solution of hydrofluoric acid; etching with a one-per-cent solution of sodium hydroxide; etching in a warm five-per-cent solution of oxalic acid; anodic pickling in a warm five-per-cent sodium-carbonate solution; and scrubbing with fine emery flour wet with water. The results of the tension tests of the corroded bars, which are given in Figure 9, together with the appearance of the corroded surfaces, which did not differ much in their general nature, indicated that, for an extended corrosion period, the method by which the specimen is cleaned prior to corrosion is only a minor factor in determining the uniformity of the surface corrosive attack.

As will be shown in a later report, however, the initial character of the surface, particularly with respect to the degree of polish, may have an appreciable effect in delaying the corrosive attack. After corrosion has once started, however, the influence of the surface characteristics is entirely negligible.

## (b) L i g h t

In a few tests, particularly in some carried out in mid-summer, the resistance of sheet duralumin to corrosive attack by the sodium chloride-hydrogen peroxide solution was unexpectedly high. In order to show whether the results were dependent in any way upon the influence of light, a number of specimens, while being corroded in the usual manner in the sodium chloride-hydrogen peroxide solution, were exposed for several hours each day to the light from a carbon arc lamp. A similar set was corroded within a light-tight cabinet and a third set corroded in diffused daylight. The results (Fig. 9) showed that the tensile properties of the specimens corroded in darkness were noticeably lower than those exposed to light during the corrosion, that is, the corrosive attack of duralumin by this solution is diminished by the action of light. Evidently this is because of the decomposition of the peroxide by the light. This conclusion is confirmed by the results reported by Rackwitz and Schmidt (Reference 6) in their investigation of the sodium chloride hydrogen peroxide test for aluminum. It is evident, therefore, that for consistent results in corrosion tests with this reagent, exposure to bright light must be guarded against and hydrogen peroxide must be added frequently to the solution if the test extends over several days. In the tests which were carried out with the sodium chloride hydrogen peroxide solution, additions of

the latter were made every three days during the duration of the test.

### (c) Temperature

In the tests which were conducted to determine to what extent corrosion of sheet duralumin may be influenced by temperature, plain chloride solutions (ammonium as well as sodium chloride) were used since such solutions are stable at the elevated temperature used, whereas the sodium chloride-hydrogen peroxide solution is not. The tests were carried out at 70°C (158°F.), the specimens and solution being contained within a small electrically heated oven. The results showed that the rate of attack of a very active solution, such as ammonium chloride, was not much influenced by an increase in temperature. With a less active reagent, such as sodium chloride solution, however, the rate was very appreciably greater at the elevated temperature used, being approximately four times as fast.

## IV. Tests of Alloys Differing in Composition -

### Effect of Composition

Laboratory corrosion tests were carried out on a number of alloys which differed in their composition from the typical "duralumin composition" (Table I) with the hope of showing whether or not the intercrystalline form of corrosion could be associated with any one of the elements ordinarily present in this alloy. These materials are listed in Table III. The first four are

available commercially in sheet form, the heat-treatment and properties of which have been described (Reference 7). Most of the others were prepared especially for the investigation, several of them being prepared by a manufacturer under commercial conditions. Consideration was also given to the tensile properties of the materials in order to obtain information concerning the possible use of any of these alloys in aircraft construction. It will be noted that the tensile strength of the two alloys containing beryllium are so low, as compared with duralumin, that their use would not be considered at all. Their inclusion in these tests was for another purpose, however.

The surface appearance of duralumin, after being corroded according to the method of any of the previously described tests often suggested that the presence of copper in the alloy was related to the behavior of the alloy under such corrosive conditions. The adhering white corrosion product was frequently tinged with red and the more or less isolated corrosion centers could be associated with a small reddish brown spot. This corrosion product gave a pronounced test for copper when tested chemically.

TABLE III. Sheet Alloys Used in Corrosion Tests Which Differed in Composition from the Usual Duralumin (Table I).

Designation of Material	General Nature of Material
25S	Commercial alloy sheet (described in A.S.S.T. Handbook, data sheets Al 5601)
51S	" " " " " " " " " " " "
A-17ST	" " " " " " " " " " " "
B-17ST	" " " " " " " " " " " "
63A	Prepared by manufacturer A for this investigation, Fe content higher than in ordinary duralumin.
58B	" " " " " " " "
I-1	" " " " " " " "
I-3	" " " " " " " " Made from material of high purity, low Fe and Si contents.
I-3	Duralumin type of alloy (17S)
Y	Y-alloy, (11th - Alloys Research Report, British Inst. of Mech. Engrs.).
Al-Be, (A)	"Beryllium duralumin" - Prepared at Bureau of Standards for this investigation.
Al-Be, (B)	" " " " " " " " " " " "

TABLE III (Cont.)

Designation of Material	Composition (per cent) (b)										Tensile Properties (a)	
	Cu	Fe	Si	Mn	Mg	Ni	Pb	Ca	Sn	Zn	Ultimate Tensile Str'th lb./sq.in.	Elongation(2") per cent
25S	4.2	.45	0.9	.68	.10	n.d.		n.d.	n.d.	n.d.	25ST 59,500	25.0
51S	.05	.38	1.0	.01	.61	n.d.		n.d.	n.d.	n.d.	25SW 48,800	19.0
											51ST 49,000	13.5
											51SW 37,100	27.0
A-17ST	2.5	.38	.24	.02	.40	n.d.					43,000	19.5
B-17ST	3.7	.36	.22	.02	.45	n.d.					53,600	21.5
63A	3.8	1.15	.24	.50	.63	.02					53,200	16.0
58B	3.1	.55	.21	.50	.63	n.d.					51,800	19.0
I-1	4.2	.20	.20	.47	.47	n.d.	n.d.	n.d.	n.d.	n.d.	59,700	18.8
I-2	4.2	.08	.10	.47	.52	n.d.	n.d.	n.d.	n.d.	n.d.	61,500	18.5
I-3	4.2	.47	.34	.47	.50	n.d.	n.d.	n.d.	n.d.	n.d.		
Y	4.1	.25	.20	.01	1.56	1.9	n.d.	n.d.	n.d.	n.d.	59,900	16.0
Al-Be, (A)	.05	.09	.14	n.d.	1.2	(Be=0.8)		n.d.			29,300	18.0
Al-Be, (B)	.05	.08	.8	n.d.	n.d.	(Be=0.4)		n.d.			28,500	11.5

(a) All materials in heat-treated condition.

(b) Analyses by J. A. Scherrer, Chemist.

Archer and Jeffries (Reference 8) have described two high-strength aluminum alloys, the development of which was based upon the assumption that the age-hardening properties of duralumin are attributable to the presence of two constituents in this material, one,  $\text{CuAl}_2$  and the other  $\text{Mg}_2\text{Si}$ . The material designated as 25S in Table III is the alloy described by Archer and Jeffries as the one which owes its superior strength when heat-treated, principally to the presence of  $\text{CuAl}_2$ , and the material, 51S, to  $\text{Mg}_2\text{Si}$ . Both of these materials are commercially available in two heat-treated conditions (designated by T and W). Numerous laboratory accelerated corrosion tests were carried out on these two materials (25S and 51S), the results of which are summarized in Figure 10. These results confirm the conclusion based upon the results of tests of duralumin, that chlorides are by far much more corrosive than any of the other common solutions and that the attack of a chloride solution can be decidedly accelerated by the presence of an oxidizer. In making any comparison of the corrodibility of the two materials, consideration must be given to the heat treatment. Specimens marked T were subjected to accelerated aging, that is, in the commercial heat treatment, after quenching, the material was heated in order to permit the structural change known as "aging" which results in the hardening and strengthening of the material, to occur. In duralumin this change occurs at room temperature. As will be shown in another report, aluminum alloys of the type which respond

to heat treatment are less resistant to corrosion in those cases in which accelerated aging is used than when aged at room temperatures. This effect must be given consideration in any comparison made of the relative corrosion resistance of the materials 25S and 51S. The results of the corrosion tests (Fig. 10) show that in the quenched state (W condition) the copper bearing alloy had a very much lower resistance to chloride corrosion than the corresponding magnesium-silicon alloy (51S). The effect of accelerated aging in both alloys (T condition) was to increase their susceptibility to corrosive attack. The examination of the structure of the corroded specimens indicated, in general, a greater intercrystalline attack in the copper bearing alloy (25S) than in the other one (51S). This is illustrated in Figure 11.

Two other commercial alloys used in the corrosion tests are those designated as A 17S and B 17S (Table III) (Reference 9). Both of these alloys are of very low manganese content (.02 per cent) and A 17S has, in addition, a considerably lower copper content than occurs ordinarily in the usual duralumin type of alloy. The behavior of the B 17S when corroded (Fig. 12) was not essentially different from that of the ordinary duralumin composition under the same conditions. A 17S showed a higher corrosion resistance which, in all probability, can be attributed to its lower copper content. However, on account of the initially lower tensile properties of this sheet material as

compared with the usual duralumin sheet it cannot be considered for replacing the latter except for certain special uses. Evidently, as shown by the behavior of these two materials as compared with that of material having a much higher manganese content, the element manganese should be regarded as having no marked effect in determining the susceptibility of the duralumin type of alloy to corrosion.

The material designated as 63A was prepared by one of the cooperating manufacturers under commercial conditions with an iron content much higher than is ordinarily found in this material. The results obtained, when the material was corroded with sodium chloride (Fig. 12), suggested a somewhat more rapid attack than was ordinarily the case for duralumin with the usual iron content. The behavior of material  $I_2$  which had a relatively very low iron content, however, did not indicate that iron is to be regarded as contributing to any very appreciable extent to the susceptibility to corrosion.

Material 58B was intended as a low-copper duralumin. The copper content, 3.1 per cent, was not so low, however, as that of one of the other materials, referred to above, (A-17ST). In other respects 58B did not differ essentially from the typical duralumin composition. When corroded with a chloride solution, it did not show any very decided improvement in corrosion resistance over that of heat-treated duralumin of the usual composition.

In the preparation of material  $I_2$ , which was done under

commercial conditions by one of the cooperating manufacturers, aluminum of very much higher purity than is ordinarily used for this purpose was employed. The alloy, as a result, had a relatively very low iron content and also a silicon content much below that ordinarily found in duralumin. Material  $I_1$  was submitted by the same manufacturer as representative of an alloy which seemed to have shown some promise in their tests of having corrosion-resisting properties superior to those of the usual grade of duralumin. In preparing this material, consideration was given the two impurities, iron and silicon. The iron content was considerably lower than is ordinarily the case with duralumin and the silicon was also lower than is the case in most duralumin (Table III, alloy  $I_3$ ). The results of the laboratory corrosion tests did not indicate any pronounced superior corrosion resistance of this material over the ordinary duralumin composition, provided all had received essentially the same heat treatment. In carrying out the corrosion tests on these two materials,  $I_1$  and  $I_2$ , a third one, designated as  $I_3$  in Table III, was used throughout for comparison. This was an alloy of the ordinary duralumin composition (17S) furnished by the manufacturer along with the other two.

The material designated as "Y alloy" (Table III) has been described by Rosenhain (Reference 10) and, in addition to containing the alloying elements present in duralumin, in amounts equal to those found in duralumin, contains nearly 2 per cent of

nickel. This material was found to be very susceptible to intercrystalline corrosion when corroded in a chloride solution. However, since accelerated aging is necessary for developing the highest tensile properties of this alloy by heat treatment, it is probable that the susceptibility to attack is to be attributed to this rather than to the presence of nickel.

The two alloys Al-Be(A) and Al-Be(B) were prepared at the Bureau of Standards for the investigation, copper being omitted from the alloys and beryllium used as an alloying element along the lines described by Kroll (Reference 11). In one case (A), Kroll's suggestion that in such an alloy a compound of beryllium and magnesium might be formed which might act as the hardening constituent in heat treatment and in the other (B) Corson's (Reference 12) suggestion of the formation of a compound of beryllium and silicon were the bases for the compositions chosen. The tensile properties of both of these materials in the heat-treated sheet form were found to be very much inferior to those of duralumin and, hence, their use as a substitute for duralumin is not practicable. Their behavior under corrosion conditions is of interest, however. The change in the tensile properties was very considerably less than in duralumin under corresponding conditions and no evidence, whatsoever, of any intercrystalline attack was shown by either after being corroded.

A method for the improvement of aluminum alloy castings,

particularly by rendering them less porous, has been favorably reported upon (Reference 13), as a result of an investigation carried out at the National Physical Laboratory. Essentially the method consists in allowing the temperature of the furnace holding the molten metal to drop slowly so as to permit the metal just to freeze, thus expelling most of the "dissolved gases" which it might contain. The metal is then heated up to the proper temperature and poured in the usual manner.

A small heat of duralumin prepared at the Bureau of Standards, a portion of which had been treated according to this method and the remainder of which was poured into ingot form without any special treatment, was rolled into sheet form for corrosion tests. As shown in Figure 12, both lots of materials behaved essentially the same; the "degasifying" treatment did not seem to have any influence so far as the corrodibility of the resulting sheet was concerned.

The general conclusion concerning the effect of composition upon the corrosion of duralumin is that, of the various elements present, copper is most closely related to the susceptibility of this material to intercrystalline corrosion. No clear and definite relation between the other elements which may be present and the corrodibility of the material could be shown to exist by the results of the corrosion tests. As will be shown in another report, however, the composition of duralumin is a factor of relatively minor importance, providing that the heat treat-

ment of the material has been carried out in a suitable manner. Some of the very low-copper materials, for example 51S, showed after severe corrosion some evidence of intercrystalline attack, a fact which supports the conclusion that the simple presence of copper in duralumin is not a complete and satisfactory explanation of the intercrystalline type of corrosion of this material.

Sheet aluminum either of very high purity or of ordinary commercial grade, is not subject to intercrystalline corrosion. The disintegration of aluminum sheet by intercrystalline corrosion observed a number of years ago by foreign metallurgists, for example, LeChatelier (Reference 14), can be ascribed to the impurities often present in aluminum as made at that time. A case of disintegration in service of an aluminum alloy reported by Seligman and Williams (Reference 15) is of decided interest in connection with the tests reported above. Wire screens which had been used for several years for supporting thin slabs of gelatine, which was said to be free from all chemicals except small quantities of hydrogen peroxide, in some cases showed complete intercrystalline disintegration, whereas other screens were in good condition after the same length of service. The deteriorated wire was found to have a composition as follows:

Silicon	0.33 per cent
Iron	0.30 "
Copper	2.65 "
Aluminum by difference,	96.72 per cent

The composition of the wire which showed no disintegration was:

Silicon	0.24 per cent
Iron	0.22 "
Copper	0.07 "
Aluminum by difference,	
	99.47 per cent

The reason for the deterioration is apparent.

#### V. Microstructural Aspects of Corroded Duralumin

In structure, the alloys of the duralumin type consist of a relatively soft aluminum-rich matrix throughout which are disseminated a host of particles of the harder constituents which result from the presence of the alloying elements, copper, magnesium, iron, etc. Essentially, these constituents in duralumin are of three kinds, one resulting from the combination of copper and aluminum,  $\text{CuAl}_2$ , another,  $\text{Mg}_2\text{Si}$ , and a third, the exact composition of which has not been fully determined, is an iron compound which is sometimes associated with free silicon. Since iron is present in the alloy as an impurity and so far as is known serves no very useful purpose in attaining the characteristic properties of duralumin, this constituent may be regarded as a more or less incidental one. The distinguishing of the various constituents from one another is most readily done in specimens of the cast material. The identification of the different constituents which, in the cast alloy, are associated together and form a supporting or "skeleton" network is best done at rather high magnification and depends upon the

appearance of the different ones in the unetched state and their response to various etching treatments. These constituents are depicted in Figure 13.

As a result of the severe mechanical deformation which is necessary in order to put the material into sheet form, together with the accompanying annealings, the structural appearance is completely changed from that of the cast metal. The copper-bearing and the iron-bearing constituents which occur in much smaller and more rounded particles are found distributed throughout the recrystallized matrix in a rather haphazard manner, the only semblance of order being a somewhat streaked arrangement which coincides with the direction of rolling and is determined by it. The magnesium silicide constituent cannot be identified with certainty in sheet duralumin. Figure 14 illustrates the characteristic appearance of sheet material of the duralumin type of alloy.

A great many observations have been made to determine whether the intercrystalline type of corrosion attack can be associated with and, hence, attributed to, some special or unusual structural feature such as, for example, films of one or more of the alloy constituents which might envelop the grains. In a few cases a suggestion of this has been noted but adequate and consistent evidence of this in materials which develop intercrystalline corrosion under favorable conditions has not yet been found. It appears therefore that this type of corrosion is to be

attributed primarily to some structural feature or condition which is not revealed by ordinary microscopic examination.

## VI. Other Tests of Corroded Sheet Duralumin

### 1. Electrical Resistivity

The desirability of a method of examination which might be used to show the progress of any corrosive attack of a built-up duralumin structure without, however, cutting or disturbing it in any way is very evident. The determination of the change of electrical resistivity accompanying corrosion of the intercrystalline type suggests itself as a possibility along this line. The results of a number of determinations of this kind (Reference 16) on specimens, the tensile properties of which were afterwards determined, are summarized graphically in Figure 15. It will be seen from these results that although intercrystalline corrosion, as induced by accelerated corrosion in the laboratory, resulted in an increase in electrical resistance of the material, the accompanying decrease in the tensile properties, especially in the elongation, was of a much higher magnitude. Thus in the most severely embrittled specimen, a decrease in elongation of approximately 80 per cent was accompanied by an increase in electrical resistance of only about 6 per cent, the variation in the resistance of the uncorroded bars being of the order of 2.5 per cent. The determination of electrical resistivity does not appear to be very useful, therefore, as an inspection test

for estimating with any degree of accuracy the extent of intercrystalline corrosion and the resulting deterioration of the material in its tensile properties.

## 2. X-Ray Determination of Crystal Structure

Clark's statement (Reference 17) that "Duralumin samples which show maximum tendency to intercrystalline corrosion, a phenomenon of possible importance in light of the disaster of the Shenandoah whose frame was duralumin, invariably are distinguished from their X-ray patterns by greater internal strain and by a recrystallization or slow aging process under strain" suggests that examination by the X-ray method ought to yield very useful and helpful results in the study of the corrosion of sheet duralumin. Differences, such as were referred to by Clark, in the X-ray patterns of sheet duralumin as determined by the "pinhole" method (Laue method) of X-ray examination are depicted in Figure 16, 'b' being the pattern which has been said to result from the intercrystalline embrittled condition.

A very considerable number of specimens of sheet duralumin representative of material which had been used in service, material attacked in an intercrystalline manner by accelerated corrosion methods in the laboratory, as well as sheet which after a known period of exposure to the weather showed intercrystalline attack, together with uncorroded specimens which had been heat-treated in such a manner as to render some very

resistant to intercrystalline corrosive attack and others very susceptible to it (as proved in each case by both laboratory and exposure tests) were examined by the X-ray method. The results, which will be described in greater detail in another publication, will only be summarized here. In brief, these results do not support Clark's general conclusion that duralumin sheet which is especially susceptible to intercrystalline corrosion can invariably be distinguished by its X-ray pattern.

Of 18 specimens representative of sheet duralumin which had been used in aircraft construction and of which 8 showed a distinct X-ray pattern similar to that of Figure 16,b only one was found to have undergone intercrystalline corrosion as shown by an examination of the microstructure. Specimens of heat-treated sheet duralumin which had been corroded in the laboratory and had shown distinct evidence of an intercrystalline attack showed no marked resemblance in their X-ray pattern to Figure 16,b whereas heat-treated sheet duralumin which had been cold-rolled prior to corrosion, did to some extent. Sheet material which in heat treating it, had been quenched in hot water could not invariably be distinguished by the X-ray pattern from similar material which had been quenched in cold water, although, as will be shown in another report, sheet duralumin heat-treated in these two ways differ very decidedly in their susceptibility toward intercrystalline corrosion. X-ray examination of duralumin including some large crystals of dura-

lumin which had been deformed by cold rolling gave results which supported Clark's conclusion to the extent of showing that the unusual type of X-ray pattern of these materials is related to the "greater internal strain" of such material. Although such a condition of internal stress in duralumin may be regarded as a favorable one for the occurrence of intercrystalline corrosion, it is very far from being an established fact that this is the fundamental cause of this phenomenon. The X-ray method of examination is therefore limited in its applicability and should be regarded as a useful means for demonstrating the existence of internal stresses, a condition which may help to make duralumin somewhat more susceptible toward intercrystalline corrosion, rather than showing what the fundamental condition for this behavior really is.

## VII. General Value of Corrosion Tests

Accelerated laboratory corrosion testing methods in general are valuable for what they indicate rather than for what they prove. Such accelerated tests are, however, intended to reproduce the essential conditions which contribute toward the service behavior of the material and, hence, to give an indication of the probable behavior in service of the material. The above-described tests of sheet duralumin are to be regarded in this light, that is, as "pilot tests" indicating the probable behavior of the material in service. Tests of the same materi-

als under conditions more perfectly comparable with service conditions, that is, for this material, weather-exposure tests, are necessary as a supplement either to confirm or possibly to refute the conclusions which the laboratory tests seem to warrant. Extensive weather-exposure tests are now under way and will be described later as the results become available.

The question whether either static stress or repeated stress acting simultaneously with corrosion may not accelerate the rate of attack is also being studied and will be reported on later.

#### VIII. Summary

1. This report is concerned with the permanence, with respect to corrosion, of light aluminum alloy sheets of the duralumin type, that is, heat-treatable alloys containing Cu, Mg, Mn, and Si.

2. The corrosion of aluminum alloys of the duralumin type, may manifest itself in two different ways. In one of these, the attack is a surface one only and, being usually nonuniform in its distribution, results in a roughening (pitting) of the surface. This is analogous to the familiar rusting of iron. In the other, the corrosive attack is not restricted to the surface of the material but penetrates into the body of the metal, the path by which it progresses inwardly being an intercrystalline one.

3. By corrosion, the tensile load necessary to break a specimen is, in general, reduced to the same extent that the effective cross section is reduced by the corrosive attack. After corrosion of duralumin according to the first type, the change in cross-sectional dimensions can usually be readily determined. After an attack of the second type, however, especially in sheet material, the effective cross section may be only a small fraction of the initial value and the breaking load may be correspondingly low, although the external appearance gives no true indication of such a pronounced change. The elongation (ductility) of the sheet material is usually reduced by intercrystalline corrosion to a greater degree than is the ultimate tensile strength, this being ascribed to the "notch effect" of the deeply penetrating corrosion fissures.

4. In the determination of the effect of intercrystalline corrosion on the tensile properties of sheet duralumin, it is essential that the tests be carried out on full-size tension specimens. Little, if any, useful information in such a case, would be gained from the ordinary loss-of-weight corrosion tests. The change in the tensile properties forms a dependable criterion of the magnitude of the corrosive attack.

5. Laboratory corrosion tests were carried out by the intermittent repeated immersion method, the specimens being momentarily dipped into the corrosive solution once every 15 minutes

and then withdrawn and allowed to dry off in the air. Such a method was thought to be more representative of conditions obtaining in aircraft service than a continuous immersion would be. It was found to give significant results in a considerably shorter time than the "spray" test does. Microscopic examination of corroded specimens was made to determine the nature of character of the attack.

6. An intercrystalline attack was induced in sheet duralumin by corroding specimens in this manner in a chloride solution, (calcium or sodium chloride). The addition of an oxidizing agent, such as hydrogen peroxide, was found to accelerate the corrosive attack very materially. Other halogen solutions (bromides and iodides) were found to behave similarly to a chloride solution though at a somewhat slower rate. Ammonium chloride solution was found to be very active even without the addition of any oxidizer. Other common solutions, nitrates, sulphates, and carbonates, even with an oxidizer present were found to have no appreciable corrosive effect on duralumin and to cause no intercrystalline attack, whatsoever.

7. Of the various alloying elements in duralumin including those such as iron, which are present as impurities rather than intentional additions, copper appears to be most closely associated with the propensity of the material toward intercrystalline corrosion. Other factors, however, especially the method of

heat treatment are of decided importance in determining the behavior of the material with respect to corrosion. Under some circumstances, some alloys of very low copper content were found to corrode in an intercrystalline manner. The attack in such cases, however, was less severe than that of an alloy of higher copper content.

8. The specimens subjected to accelerated corrosion tests in the laboratory always showed a more or less "spotty" appearance after corrosion. The intercrystalline attack was most severe under the "spots" or surface accumulations of corrosion products. The method by which the specimens were cleaned prior to corrosion does not appear to be the deciding factor in causing this nonuniform corrosion attack.

9. Accelerated corrosion tests made at an elevated temperature in which a very active solution was used, did not differ in their results from tests made at room temperature. With more mildly acting solutions, however, the corrosion rate was increased approximately fourfold by using a temperature of  $70^{\circ}\text{C}$ .

10. In structure, aluminum alloys of the duralumin type consist of a relatively soft aluminum-rich matrix; throughout which are disseminated the particles of the harder constituents resulting from the presence of the alloying elements. The deformation which is necessary for putting the material into sheet form re-

sults in the fragmentation and redistribution of these particles of the alloying constituents. The intermediate annealings during the working of the material, together with the final heat treatment of the sheet changes the form and size of the particles, particularly of certain compounds, as they are dissolved in solid solution in the matrix. No regularity exists in the distribution of the particles of the harder constituents throughout the microstructure sheet, other than a streakiness resulting from the rolling which varies in degree in various portions of the cross section of a sheet and from sheet to sheet. No distinct evidence of a structural condition at the grain boundaries which would definitely account for the intercrystalline corrosive attack has yet been found in the microstructure of duralumin sheet. Some slight evidence of  $\text{CuA}$  at the grain boundaries in film-like form as seen at rather high magnification has been noticed but the evidence is so fragmentary that no general conclusion is warranted.

11. Electrical resistance measurements made on specimens after progressively increasing amounts of corrosion have not given results which would warrant the use of this method as a "non-destructive" inspection method.

12. X-ray examinations by the "pinhole" (Laue) method do not afford a sure means for distinguishing sheet duralumin which is very susceptible to intercrystalline corrosion from that which is not.

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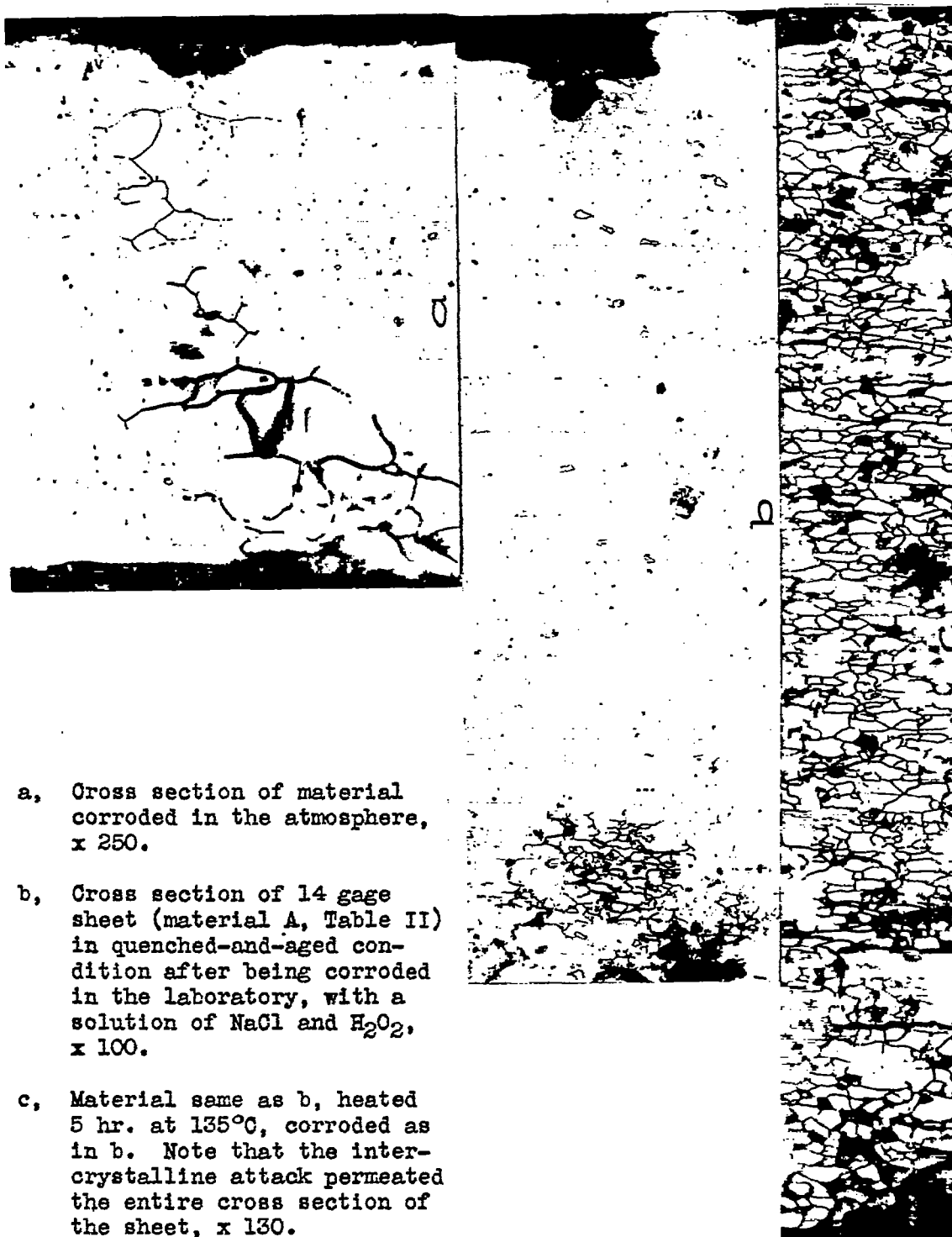


Fig. 1 Microstructure of sheet duralumin after intercrystalline corrosion; unetched.

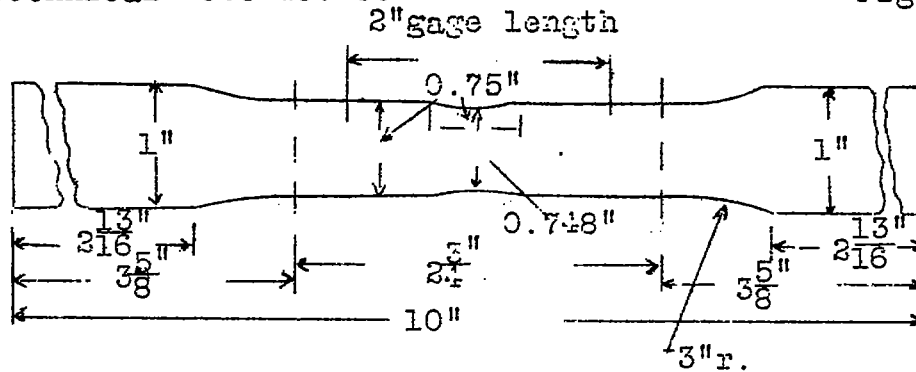


Fig.2 Dimensions of tension specimen used in all the corrosion of this and succeeding reports.

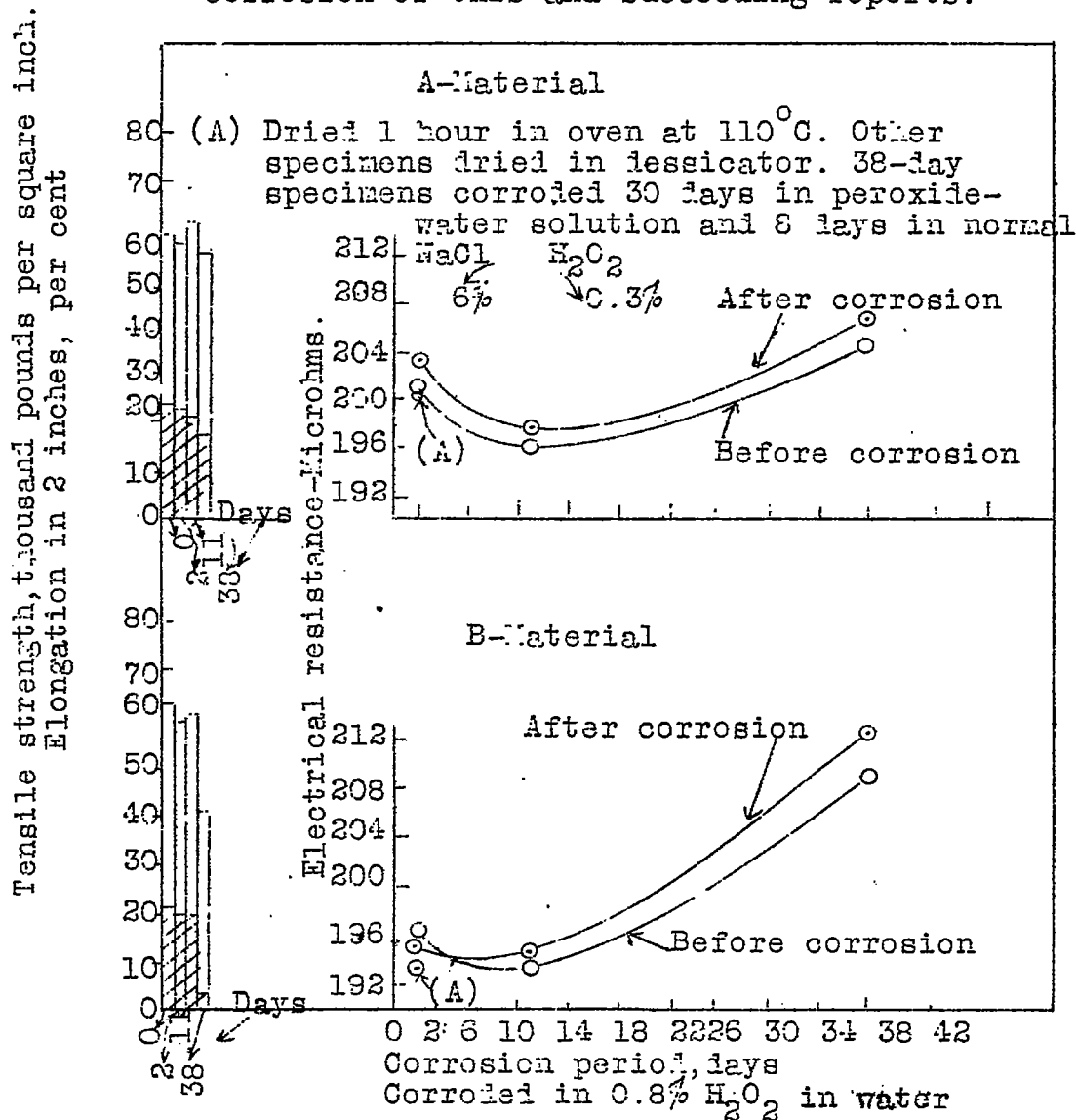


Fig.15 Comparative effect of corrosion on the electrical resistance and tensile properties of sheet duralumin.

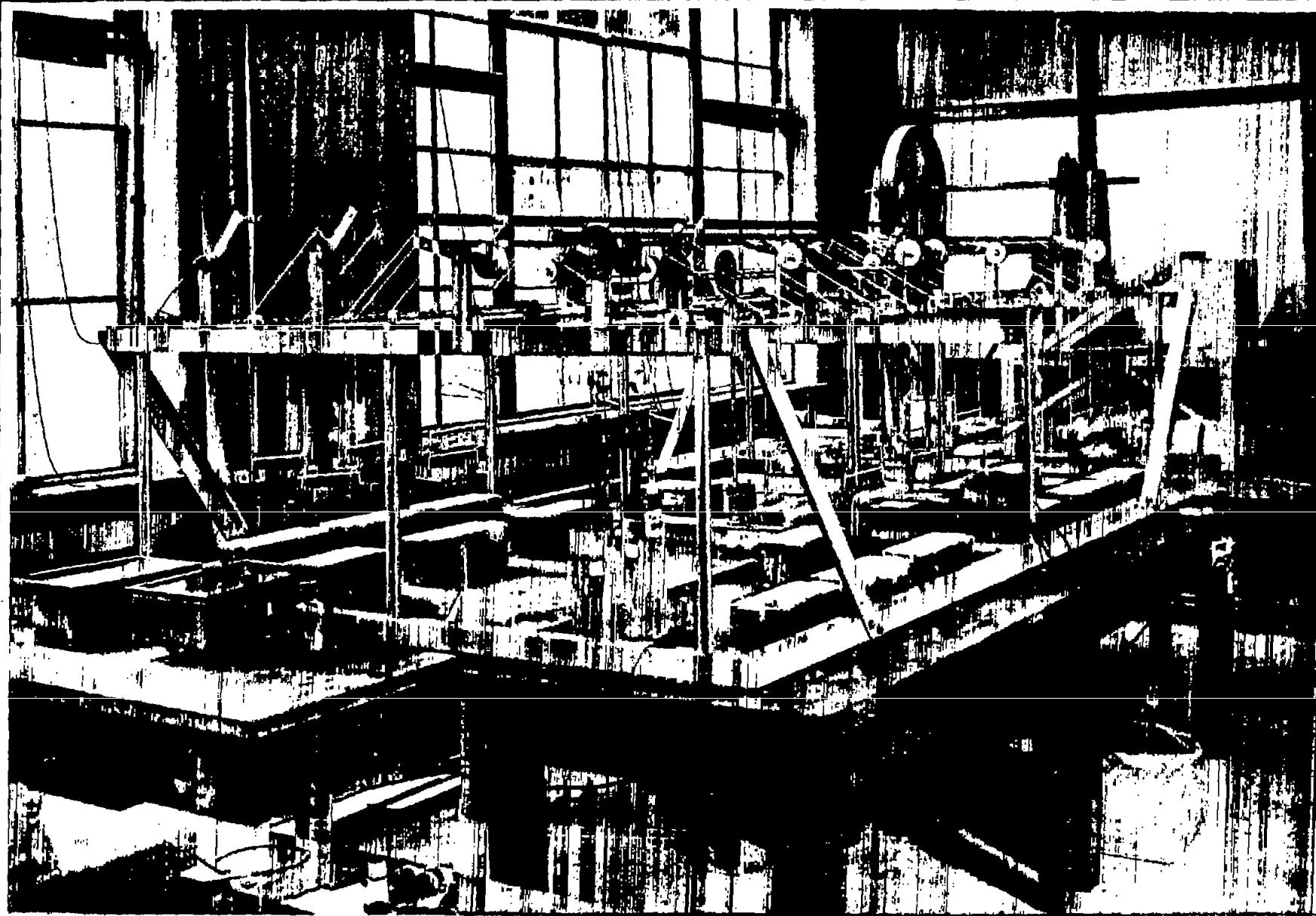


Fig. 3 Apparatus used in repeated immersion corrosion tests  
(wet and dry tests).

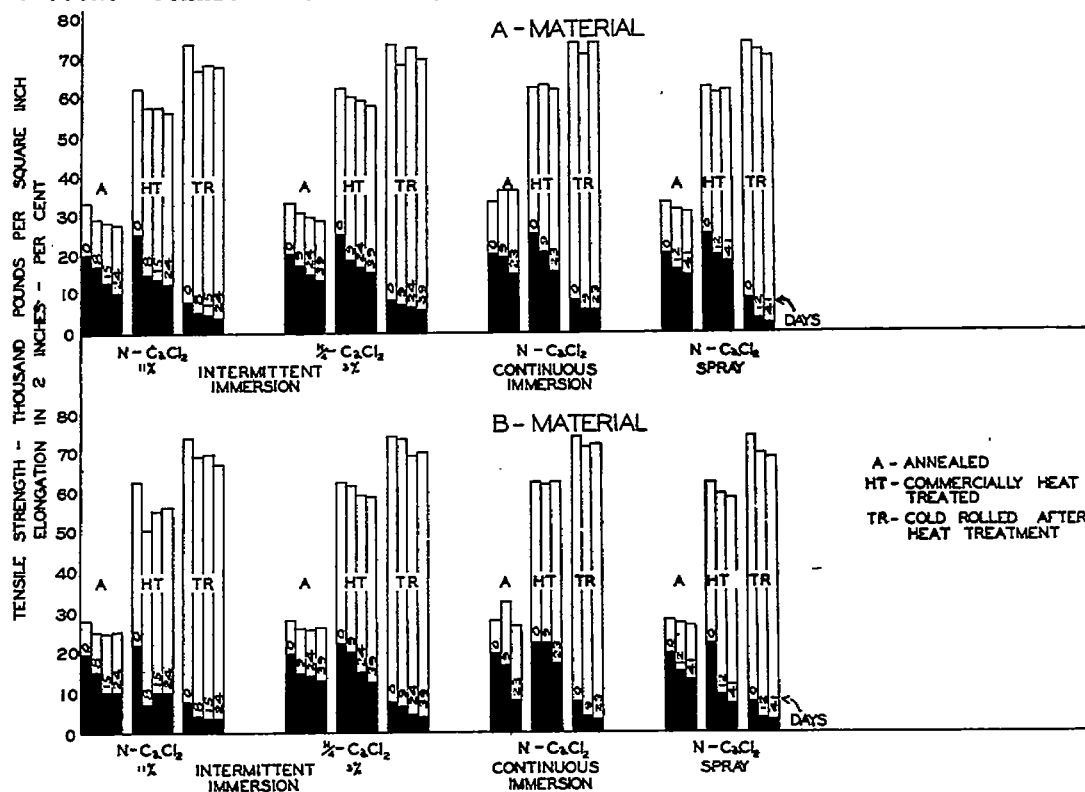


Fig. 4

Effect of corrosion by calcium chloride solutions on sheet duralumin.

In this and succeeding figures, the ultimate tensile strength of the material is shown by the total height of the rectangle; the elongation by the

height of the shaded rectangle. All sheet material was 14 gage unless stated otherwise. The concentrations of solution (here and elsewhere) expressed by per cent, are only approximate

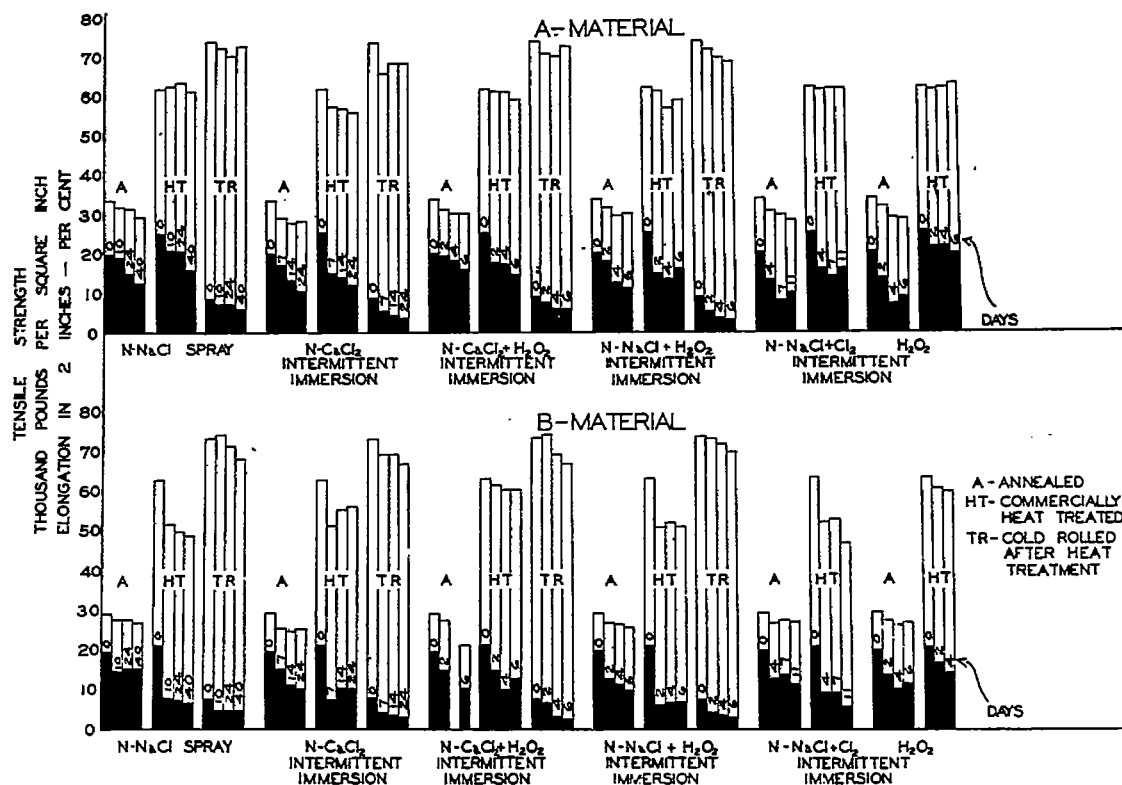


Fig. 6 Effect of corrosion by chloride solutions on the properties of commercial sheet duralumin.

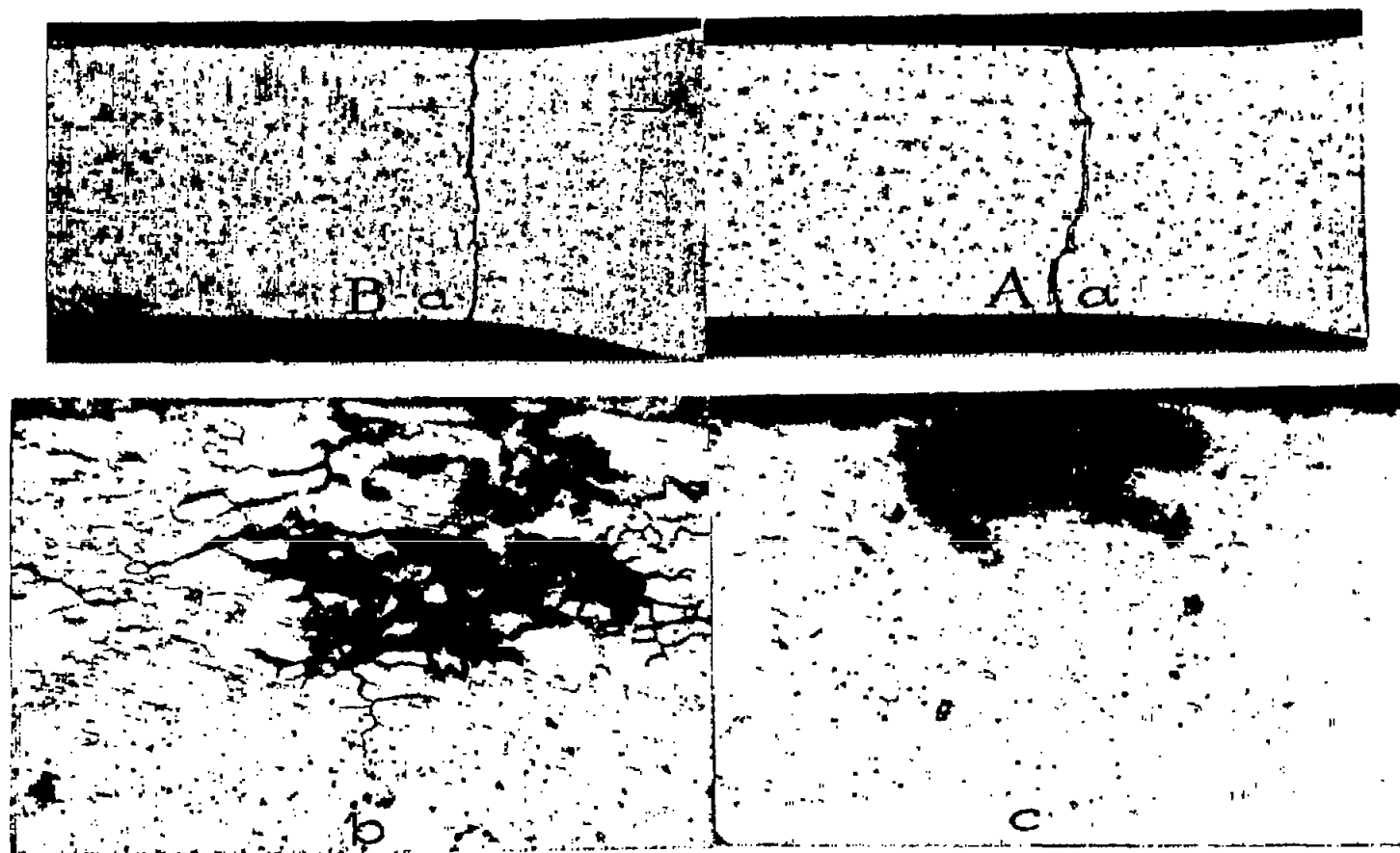
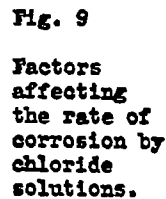
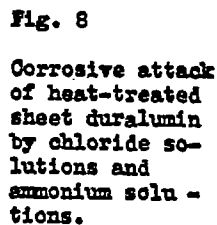
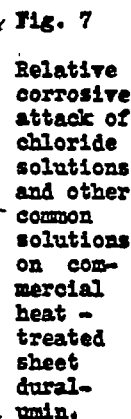
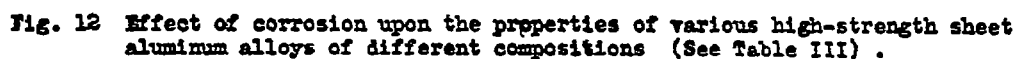
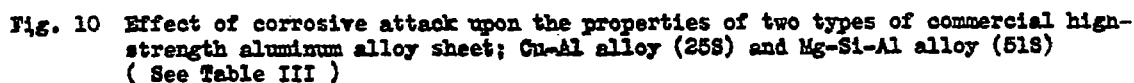


Fig. 5 Structure of heat treated sheet duralumin corroded by calcium chloride solution,  $6\frac{1}{2}$  days by intermittent immersion.

- a, Surface appearance of corroded bars,  $\times 2$ , A and B material (Table II).
- b, Microstructure (unetched),  $\times 250$  of B material under one of the corrosion areas.
- c, Same for A material; apparently in this case pitting has kept pace with any intercrystalline attack which took place.





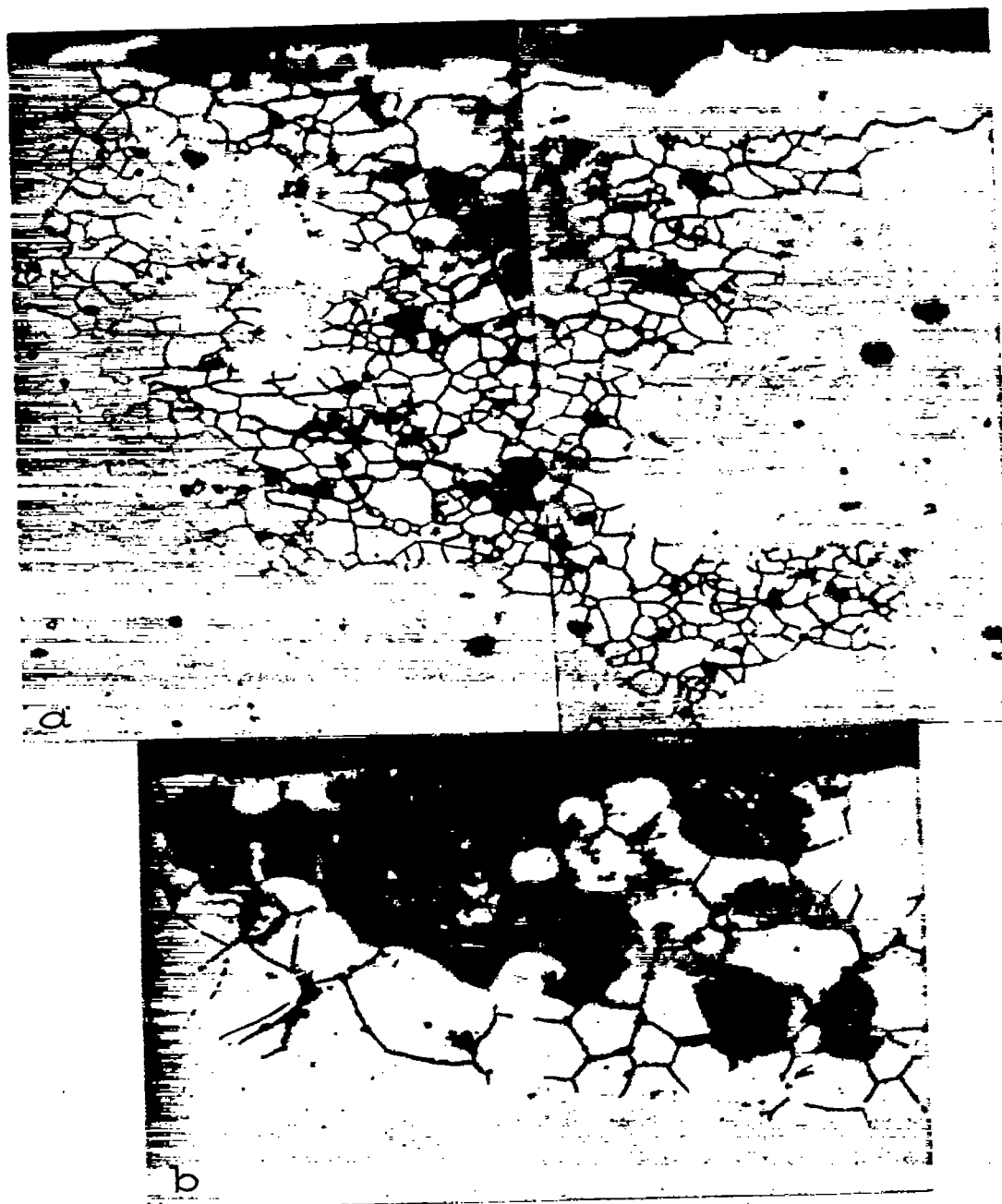


Fig. 11 Effect of corrosion on the structure of the material of Figure 10. The attack after 6 days corrosion in  $\text{NaCl} + \text{H}_2\text{O}_2$  was intercrystalline in character. This was very much more pronounced in the alloy (25S) containing copper (a) than in the other (51S) (b)  $\times 250$ , unetched.

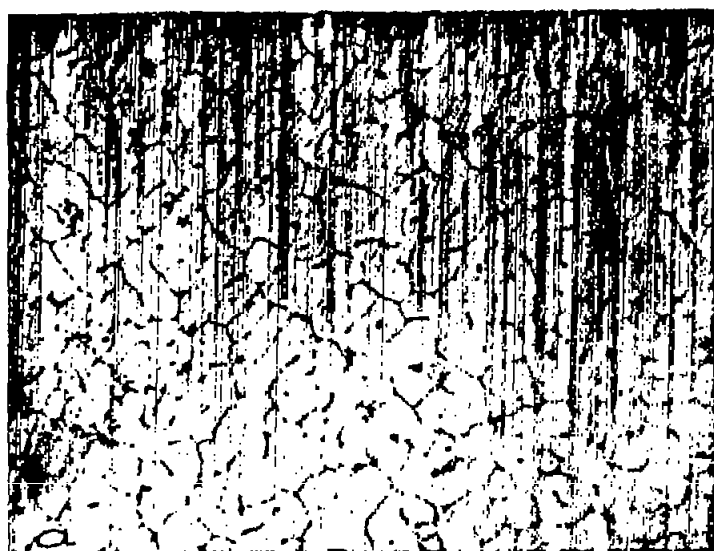


Fig. 13 Microstructure of duralumin in cast state. (A, Table I). The constituents are more readily recognized in this condition than after the material has been rolled.

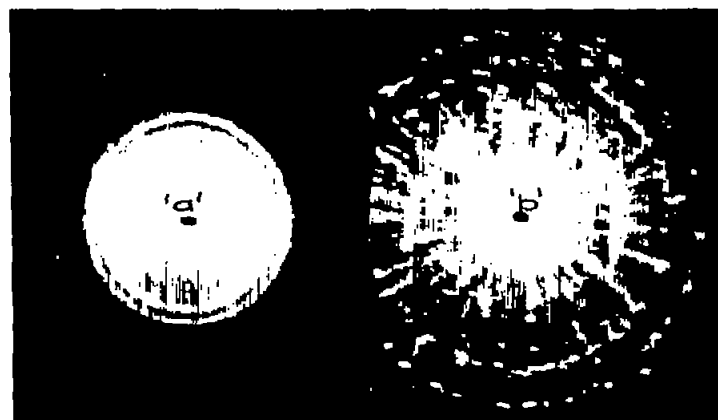


Fig. 16 X-ray patterns by the "pin-hole" (Laue) method of two samples of sheet duralumin from the Shenandoah.

Neither one showed any evidence of intercrystalline corrosion in its microstructure. Both had been in service the same length of time.

- a. Etchant 1% HF,  $\times 150$
- b. Same,  $\times 1000$ . The small dots are undoubtedly the  $Mg_2Si$  constituent.
- c. Same,  $\times 1500$ , Etched by "nitric acid quench". The dark colored constituent is  $CuAl_2$ , the other is the complex iron constituent.



Fig. 14 Microstructure of sheet duralumin and related sheet alloy sheet before and after corrosion. a, Heat treated sheet duralumin (A, Table I). b, Heat treated alloy 51ST (Table III). c, Heat treated duralumin (I-1, Table III). a, b, & c; Uncorroded sheet; etchant, 1% HF, x 250. d, Heat treated alloy sheet; 25SW (Table III), 4 days accelerated corrosion; x 1000. e, Sheet duralumin corroded in service, etched with 1% HF to reveal the grain boundaries, x 250. f, Same, x 1000. No structural features serving to direct the course of the corrosive attack are visible.